

# Permeability of Plastic Films to Methyl Bromide: A Comparative Laboratory Study

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**Abstract:** The permeability of plastic films to the fumigant methyl bromide (MB) was measured by two different methods, in order to facilitate the selection of films which are impermeable to the gas. Polyethylene-based films are highly permeable to MB, as evidenced by both methods. In contrast, multilayer coextruded films which have a layer of barrier material such as polyamide (PA) or ethylene-vinyl alcohol copolymer (EVOH) were significantly less permeable to MB, as reflected by the parameters permeability rate, time to 90% concentration (TC<sub>90</sub>, by the diffusion method) and lag-time values (by the variable-volume method). A significant correlation was found between the permeability rate assessed by the diffusion method and that obtained with the variable-volume method. Permeability of all films increased with temperature as evidenced by all tested parameters. This increase was more pronounced with polyethylene films, the permeabilities of which increased five- to six-fold when the temperature was increased from 20°C to 60°C. The effect of temperature on barrier-film permeability was less significant. Permeability of films to MB was affected by additional factors such as additives, the length of the monomer side-chain, and the thickness and density of polyethylene films. © 1998 SCI

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## 1 INTRODUCTION

Methyl bromide (MB) is the major pesticide used for soil fumigation in intensive agriculture, as well as for commodity and post-harvest quarantine treatments.<sup>1</sup> This fumigant is unique among pesticides because of its broad spectrum of biocidal activity and its ability to penetrate soils and commodities, due to its high vapour pressure. However, concern regarding its possible role in ozone depletion<sup>1</sup> and the issuance of regulations to

reduce its consumption or phase it out altogether have raised a need for the development of methods to reduce MB dosage and emission. The commonly used films for MB fumigation, e.g. low-density polyethylene (LDPE), provide a poor barrier,<sup>2–5</sup> allowing MB to escape to the atmosphere during the fumigation process. Films which are less permeable to MB could minimize this escape, thereby maintaining a higher MB concentration in the soil for a certain period, or inside a structure.<sup>6</sup> Minimizing emission would reduce the dosage without reducing the effectiveness of pest control, based upon extending pathogen exposure to the fumigant.<sup>1,2</sup>

The permeability of films to gases can be measured by a variety of standard methods which reflect different properties.<sup>5,7–11</sup> The objective of this study was to

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evaluate the effect of various factors such as barrier material, temperature and polymer composition on film permeability to MB, using two testing approaches, in an attempt to improve the selection of less permeable films which can be used for fumigation with reduced emission.

## 2 MATERIALS AND METHODS

### 2.1 Plastic films

Plastic films were obtained from various manufacturers (Table 1), and included monolayer polyolefins (i.e. LDPE and high-density polyethylene (HDPE), polypropylene and polybutylene) and multi-layer co-extruded films. The multi-layer films comprised a central layer of barrier material surrounded by layers of polyethylene copolymers. Some of the films contained metal additives or other components which were incorporated during film production, or an aluminum layer evaporated onto the already produced film, as

indicated in Table 1. All films were checked for their integrity before testing for MB permeability. The thickness of each film was measured with a special gauge, to verify producer specification. The permeability of plastic films to MB was measured by the two different methods as described in Section 2.2.

### 2.2 Film permeability

Methyl bromide permeates through plastic films by two distinct means: solution and diffusion.<sup>12</sup> If a plastic film separates two chambers, one containing MB at a high concentration or pressure, and the other MB at a lower concentration or pressure, the gas will permeate from the high pressure or concentration to the lower one in two stages. First, a 'buildup' period is observed, characterized by a slow rate of gas permeation through the film. This is followed by a second stage, in which a steady-state condition is achieved. At this stage, a linear relationship develops between time and permeability with an intercept on the time axis known as the 'lag time.'<sup>12</sup> In the linear region, Fick's first law

**TABLE 1**  
List of Films Tested for Permeability to Methyl Bromide

| <i>Number</i> | <i>Name/code</i> | <i>Thickness (μm)</i> | <i>Type<sup>a</sup></i> | <i>Manufacturer and Country</i> |
|---------------|------------------|-----------------------|-------------------------|---------------------------------|
| 1             | 38CCG            | 40                    | LDPE                    | Vistal, UK                      |
| 2             | Sedazol          | 35                    | LDPE                    | Barbier, France                 |
| 3             | None             | 50                    | LDPE                    | Unknown, Italy                  |
| 4             | None             | 30                    | LDPE                    | Unknown, Spain                  |
| 5             | Traitalfilm      | 50                    | LDPE                    | Hyplast, Belgium                |
| 6             | None             | 30 <sup>b</sup>       | LDPE                    | Ginegar, Israel                 |
| 7             | None             | 30                    | LDPE + UVA              | Ginegar, Israel                 |
| 8             | None             | 30                    | LDPE + Cu               | Constab, Germany                |
| 9             | None             | 30                    | Al coated LDPE          | Polysak, Israel                 |
| 10            | None             | 30                    | HDPE                    | Plastica Kritis, Greece         |
| 11            | Hymethyl         | 50                    | HDPE                    | Hyplast, Belgium                |
| 12            | None             | 30                    | HDPE                    | Polysak, Nir Itzhak, Israel     |
| 13            | None             | 30                    | HDPE + EVA              | Polysak, Nir Itzhak, Israel     |
| 14            | None             | 30                    | Polypropylene           | Polysak, Nir Itzhak, Israel     |
| 15            | None             | 30                    | Polybutylene            | Plastopil Hazorea, Israel       |
| 16            | Y181             | 30                    | ML (Polyamide)          | Smith Brothers, UK              |
| 17            | Bromotech        | 30                    | ML (Polyamide)          | Smith Brothers, UK              |
| 18            | AQL              | 35                    | ML (Polyamide)          | Plastico, Spain                 |
| 19            | None             | 30                    | ML (Polyamide)          | Barbier, France                 |
| 20            | Hytibarr         | 35                    | ML (EVOH)               | Hyplast, Belgium                |
| 21            | Barromide        | 30                    | ML (EVOH)               | Plastopil Hazorea, Israel       |
| 22            | Constab          | 30                    | ML (EVOH)               | Constab, Germany                |
| 23            | Sobron           | 50                    | ML (EVOH)               | Elf Atochem, France             |

<sup>a</sup> LDPE—low density polyethylene, HDPE—high density polyethylene, ML—multilayer films (indicating the barrier material) UVA—ultraviolet absorbent; Cu—copper additive; EVA—Ethylene vinyl acetate; EVOH—ethylene-vinyl alcohol. Additives of metal and other components were incorporated during film production, excluding aluminum which was coated on a produced film.

<sup>b</sup> Unless otherwise indicated in the text.

for diffusion under steady-state conditions can be applied and permeability rates can be calculated.

Two methods taken from the American Society for Testing and Materials (ASTM) standards were compared for testing the permeability of plastic films to MB: ASTM D1434, a variable-volume method,<sup>13</sup> and ASTM D3985, a diffusion method.<sup>14</sup>

### 2.2.1 Permeability of plastic films to methyl bromide using the diffusion method

Plastic permeability was determined essentially as in Kolbezen and Abu el Haj,<sup>15</sup> following ASTM D3985,<sup>14</sup> at the Laboratoire National de Protection des Denrees Stockees, Cenon, France. A stainless steel test cell (23 cm diameter) was divided into two chambers with the film under test. The plastic film was placed between the chambers, which were then fastened together to create a closed container. Methyl bromide (pure gas) was passed through the upper chamber at flow rate of 50 ml min<sup>-1</sup>. In parallel, air was passed through the lower chamber at the same flow rate. Thus, MB could reach the lower cell only by diffusion through the plastic film. The concentration of MB in the air leaving the lower chamber was determined by a conductivity cell (GowMac 20-800 gas analyzer, GowMac Instrument Co. Bridgewater, NJ) when the gas concentration in the lower cell was above 20 g m<sup>-3</sup>. When methyl bromide concentration was below 20 g m<sup>-3</sup>, gas concentration was measured by gas chromatograph equipped with a 10-m Cabowax megabore column and a flame ionization detector. The permeability ( $P$  g m<sup>-2</sup> h<sup>-1</sup>) of the film was calculated when the concentration of MB leaving the chamber reached a steady state according to eqn (1):

$$P = \frac{C \times F}{A} \quad (1)$$

where  $C$  is the MB concentration in the lower chamber (g m<sup>-3</sup>),  $F$  is the flow rate of air in the lower chamber (m<sup>3</sup> h<sup>-1</sup>), and  $A$  is the area (m<sup>2</sup>) of the tested film.

The time required for the MB concentration in the lower chamber to reach 90% of the concentration in the upper chamber was calculated and designated TC<sub>90</sub>. The value could be determined directly for permeable films (films number 1–11; Table 1). For barrier films, the TC<sub>90</sub> value was calculated by extrapolation from the permeability value obtained from the flowing tests. Films with a permeability rate lower than 1 g m<sup>-2</sup> h<sup>-1</sup> were considered as barrier films.<sup>2</sup>

### 2.2.2 Permeability of plastic films to MB using the variable volume method

This method was applied at the Laboratory for Pest Management Application, ARO The Volcanic Center, Israel following ASTM D1434.<sup>13</sup> In this method, a constant gas pressure was applied to one side of the mem-

brane, and the permeating gas was allowed to expand against a constant low (usually atmospheric) pressure. The change in volume of the permeated gas was then determined as a function of time by following the displacement of short column of liquid in a capillary. The permeability cell (CS-135, Custom Scientific Instruments, N.J. USA) consisted of two stainless steel discs (15 cm diameter) with a cylindrical cavity.<sup>16</sup> The plastic film to be tested was clamped between the two discs. The cell was supplied with an open-ended glass capillary connected in a vertical position to an opening in the centre of the upper disc. Methyl bromide (pure gas) was supplied at a constant pressure of 68.9 kPa (10 psi) to the bottom of the cell. After permeating through the membrane the gas expanded into the capillary. The assembled permeability cell was immersed in a constant predetermined temperature bath. The permeability of the plastic films to MB ( $P$ ; g m<sup>-2</sup> h<sup>-1</sup>) was determined according to Fick's law from eqn (1)

$$P = q \frac{A \Delta p}{t} \quad (2)$$

where  $A$  is the area of the film,  $\Delta p$  is the pressure differential across the film,  $t$  is the film thickness and  $q$  (g m<sup>-2</sup> h<sup>-1</sup>) is the permeability constant, which is determined from the experimental permeability data and corrected to standard temperature and pressure conditions.<sup>12,16</sup>

At the stage at which a linear relationship developed between time and permeability, regressions was performed to calculate the permeability rate and the intercept on the time axis known as the 'lag time'.<sup>12</sup> This parameter can be regarded as the breaking point when the MB has broken through the film and is transmitted from one side to the other. Films with permeability rate lower than 1 g m<sup>-2</sup> h<sup>-1</sup> and lag time over 240 min were defined as barrier films.<sup>2</sup> No transition were observed with barrier films to the second stage of gas permeability throughout the test period (4 h). Permeability for these films was therefore measured and calculated beginning 240 min from the start of the test.

## 2.3 Statistical analyses

Permeability tests for each film were repeated at least three times for each testing method. Statistical analyses of the results included calculating standard errors as indicated. Regression lines were calculated to define the relation between the permeability values resulting from the two methods and the relation between permeability parameters and the temperature. Regression lines representing the best fit of the data were drawn.

**TABLE 2**  
Permeability of Plastic Films to Methyl Bromide at Two Different Temperatures

| Number | Type <sup>a</sup> | Temperature | Diffusion method                                     |  | Variable-volume test                                 |                                |
|--------|-------------------|-------------|--|--|--|--------------------------------|
|        |                   |             | Permeability<br>(g m <sup>-2</sup> h <sup>-1</sup> ) | TC <sub>90</sub> <sup>b</sup><br>(min) | Permeability<br>(g m <sup>-2</sup> h <sup>-1</sup> ) | Lag time <sup>c</sup><br>(min) |
| 1      | LDPE              | 20          | 40.4 (±2.3)  | 60 (±2.5)                              | 11.8 (±0.2)  | 70 (±5.0)                      |
|        |                   | 60          | 221.0 (±6.6)   | 44 (±1.6)                              | 21.7 (±0.3)  | 11 (±1.8)                      |
| 2      | LDPE              | 20          | 11.9 (±1.1)  | 346 (±5.5)                             | 4.8 (±0.1)   | 85 (±7.5)                      |
|        |                   | 60          | 148.0 (±9.5)   | 58 (±2.3)                              | 13.9 (±0.2)  | 11 (±1.2)                      |
| 3      | LDPE              | 20          | 48.9 (±2.3)  | 57 (±1.6)                              | 5.2 (±0.1)   | 110 (±9.0)                     |
|        |                   | 60          | 74.9 (±3.4)  | 39 (±1.1)                              | 10.8 (±0.1)  | 11 (±0.8)                      |
| 4      | LDPE              | 20          | not tested   | not tested                             | 7.9 (±0.2)   | 75 (±5.7)                      |
|        |                   | 60          | not tested   | not tested                             | 26.4 (±0.3)  | 11 (±2.1)                      |
| 5      | LDPE              | 20          | 63.4 (±0.5)  | 56 (±2.3)                              | 3.6 (±0.1)   | 68 (±5.2)                      |
|        |                   | 60          | 254.0 (±0.6)   | 33 (±2.0)                              | 7.4 (±0.1)   | 12 (±1.2)                      |
| 6      | LDPE              | 20          | 85.4 (±0.8)  | 75 (±2.6)                              | 5.9 (±0.1)   | 60 (±3.6)                      |
|        |                   | 60          | 86.0 (±0.9)  | 22 (±1.2)                              | 18.6 (±0.5)  | 8 (±1.2)                       |
| 7      | LDPE+UVA          | 20          | 47.8 (±1.5)  | 61 (±3.6)                              | 5.1 (±0.1)   | 80 (±7.5)                      |
|        |                   | 60          | 87.0 (±1.2)  | 60 (±3.0)                              | 14.2 (±0.2)  | 15 (±2.0)                      |
| 10     | HDPE              | 20          | 34.5 (±6.0)  | 54 (±1.2)                              | 3.4 (±0.1)   | 120 (±10.0)                    |
|        |                   | 60          | 160.0 (±7.6)   | 38 (±2.6)                              | 10.8 (±0.2)  | 15 (±1.5)                      |
| 11     | HDPE              | 20          | 54.9 (±2.3)  | 92 (±4.2)                              | 5.4 (±0.1)   | 130 (±11.0)                    |
|        |                   | 60          | 91.1 (±2.5)  | 92 (±4.3)                              | 8.1 (±0.2)   | 12 (±1.9)                      |
| 16     | ML<br>(polyamide) | 20          | 0.2 (±0.01)  | > 500                                  | 0.05   | > 240                          |
|        |                   | 60          | 0.8 (±0.01)  | 100 (±2.6)                             | 0.15   | 180                            |
| 17     | ML<br>(polyamide) | 20          | 0.1 (±0.01)  | > 500                                  | 0.05   | > 240                          |
|        |                   | 60          | 0.5 (±0.01)  | 400 (±4.6)                             | 0.05   | > 240                          |
| 18     | ML<br>(polyamide) | 20          | not tested   | not tested                             | 0.05   | > 240                          |
|        |                   | 60          | not tested   | not tested                             | 0.05   | > 240                          |
| 19     | ML<br>(polyamide) | 20          | 0.3 (±0.1)   | 228 (±5.6)                             | 0.05   | > 240                          |
|        |                   | 60          | 0.9 (±0.1)   | 32 (±1.1)                              | 0.10   | > 240                          |
| 20     | ML (EVOH)         | 20          | 0.02   | > 500                                  | 0.05   | > 240                          |
|        |                   | 60          | 0.22   | 180 (±2.3)                             | 0.05   | > 240                          |
| 21     | ML (EVOH)         | 20          | <0.0005  | > 500                                  | 0.05   | > 240                          |
|        |                   | 60          | 0.03   | > 500                                  | 0.05   | > 240                          |
| 22     | ML (EVOH)         | 20          | not tested   | not tested                             | 0.05   | > 240                          |
|        |                   | 60          | not tested   | not tested                             | 0.05   | > 240                          |
| 23     | ML (EVOH)         | 20          | 0.002  | 371 (±2.3)                             | 0.05   | > 240                          |
|        |                   | 60          | 0.46   | 206 (±2.3)                             | 0.07   | > 240                          |

<sup>a</sup> LDPE—low density polyethylene, HDPE—high density polyethylene, UVA—ultraviolet absorbent, ML—Multilayer films (indicating the barrier material); EVOH—ethylene-vinyl alcohol. For details see Table 1.

<sup>b</sup> TC<sub>90</sub>—The time required for the methyl bromide concentration in the lower chamber to reach 90% of the concentration in the upper chamber. For ML films, TC<sub>90</sub> value was calculated for the steady-state system.

<sup>c</sup> Lag time—The time required for permeability rate to switch from the first stage to the second and to reach steady state of permeability.

### 3 RESULTS

#### 3.1 Comparative permeability of films using the two measurement methods

Polyethylene-based films were permeable to methyl bromide, as demonstrated by both methods (Table 2). In contrast, multilayer films with a layer of a barrier material such as polyamide (PA) or ethylene-vinyl alcohol (EVOH) were significantly less permeable, as

reflected by permeability rates, TC<sub>90</sub> and lag-time values. Permeability of polyethylene-based films at 20°C ranged from 11.9 to 85.4 g m<sup>-2</sup> h<sup>-1</sup> using the diffusion method, as compared with 0.005–0.25 g m<sup>-2</sup> h<sup>-1</sup> for the multilayer films (Table 2). EVOH-based films were less permeable than polyamide-based ones. For example, the permeability of the polyamide Y181 film was 25.6 times that of the EVOH-based Barramide film at 60°C.

When permeability rates obtained by the diffusion and by the variable-volume methods were compared, a

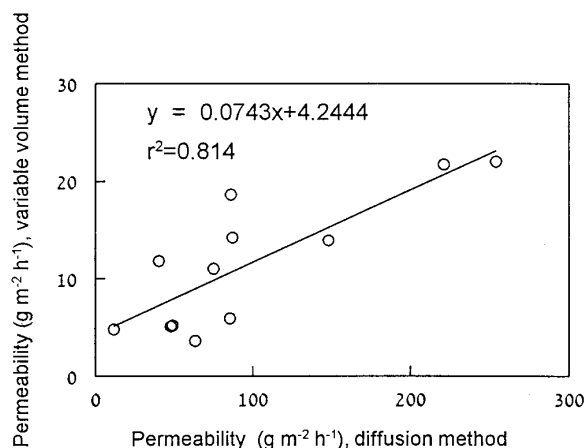


Fig. 1. Relationship between permeability to methyl bromide of polyethylene-based films determined using the diffusion and variable-volume methods.

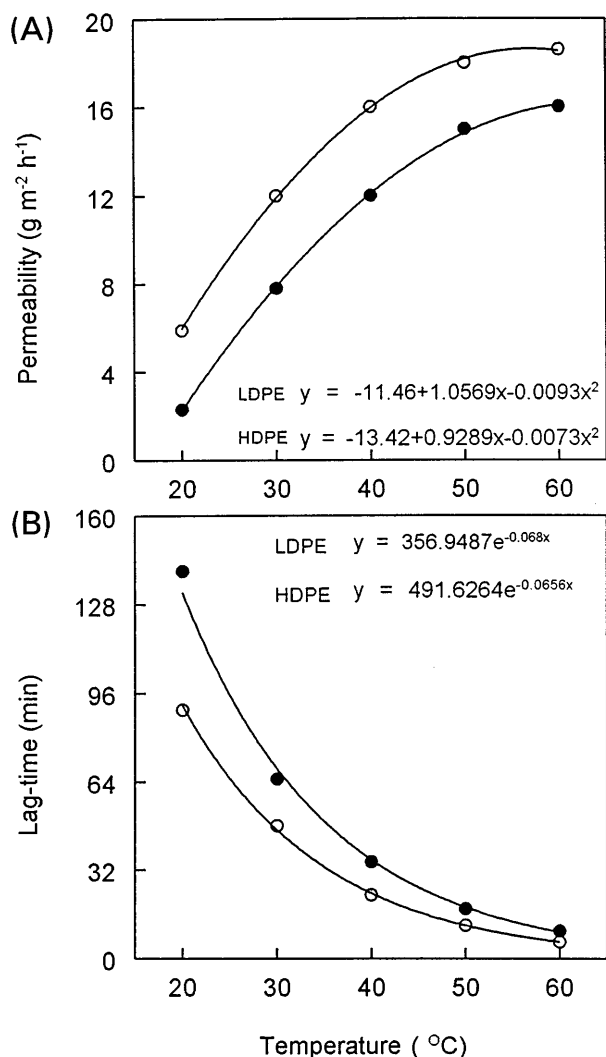


Fig. 2. Permeability of (●) high (HDPE) and (○) low (LDPE) density polyethylene to methyl bromide as affected by temperature (A). Effect on permeability (B). Effect on lag time.

significant correlation was obtained for the polyethylene-based films (Fig. 1). Although a somewhat similar trend was obtained with barrier films, the correlation ( $r^2 = 0.315$ ) was low and not significant because the variable volume method is less sensitive at low permeability rates, which are typical of barrier films. Two additional parameters, the  $\text{TC}_{90}$  value (using the diffusion method) and the lag-time value (using the variable-volume method), were determined to characterize further the permeability properties of the tested films.

### 3.2 Effect of temperature on film permeability

The permeability of all films increased with increasing temperature, as reflected by all the parameters tested (Table 2, Fig. 2). Increased permeability was especially evident with polyethylene films, where it increased five- to six-fold when the temperature was raised from  $20^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ . Thus, the permeability of HDPE was one-third of that of LDPE at  $20^{\circ}\text{C}$ , but at  $60^{\circ}\text{C}$  the relative difference in permeability was only 16% (Fig. 2A). A similar trend of temperature was also observed with the lag-time parameter. (Fig. 2B). The permeability of the barrier films at  $60^{\circ}\text{C}$  was not significantly different from that at  $20^{\circ}\text{C}$  (Table 2).

### 3.3 Effect of film composition on MB permeability

The permeability of the films to MB was also affected by additives, the type of polyolefin, the length of the monomer side-chain, and the thickness and density of the polyethylene film (Table 3). All the polyolefin films tested were more permeable to MB relative to the barrier films, yet evidently there were significant differences in permeability among the films. The length of the side-chain of the monomer affected permeability (Table 3). Thus, permeability of polybutylene films was the lowest among the polyolefins, in contrast to the high permeability of polyethylene. Polypropylene exhibited intermediate permeability values (Table 3).

The addition of metal ingredients to polyethylene decreased the permeability of these films to MB (Table 3). Aluminum coating was a more effective barrier than copper incorporated into the film. Increasing concentration of copper reduced film permeability. At increased thickness, LDPE permeability decreased (Table 3).

## 4 DISCUSSION

Since 1992 when MB was listed in the Montreal Protocol as an ozone-depleting substance, intensive efforts have been made to minimize its emission to the atmosphere. Methyl bromide, like other gases, can permeate

**TABLE 3**  
Permeability of Plastic Films to Methyl Bromide as Affected by Additives and by Thickness

| Number | Type <sup>a</sup> | Additive <sup>b</sup> | Additive (%) | Thickness (μm) | Lag time (min) | Permeability (g m <sup>-2</sup> h <sup>-1</sup> ) |
|--------|-------------------|-----------------------|--------------|----------------|----------------|---|
| 6      | LDPE              | None                  | 0            | 30             | 8 (±0.5)       | 15.7 ± 0.2  |
|        |                   |                       |              | 70             | 28 (±2.0)      | 12.8 ± 0.5  |
|        |                   |                       |              | 150            | 45 (±5.0)      | 5.5 ± 0.2   |
| 8      | LDPE              | Cu                    | 1            | 30             | 10 (±1.0)      | 5.7 ± 0.1   |
|        |                   |                       | 2            | 30             | 12 (±1.5)      | 5.9 ± 0.1   |
|        |                   |                       | 3            | 30             | 15 (±1.0)      | 5.4 ± 0.1   |
|        |                   |                       | 4            | 30             | 25 (±1.8)      | 4.0 ± 0.1   |
|        |                   |                       | 5            | 30             | 33 (±3.0)      | 2.3 ± 0.1   |
|        |                   |                       | 6            |                | 35 (±3.0)      | 2.3 ± 0.1   |
| 12     | HDPE              | None                  | 0            | 30             | 18 (±1.2)      | 18.0 ± 0.1  |
| 12     | HDPE              | Cu                    | 2            | 30             | 30 (±2.5)      | 2.1 ± 0.1   |
|        |                   |                       | 3            | 30             | 45 (±3.5)      | 2.1 ± 0.1   |
| 9      | HDPE              | Aluminum              | 0.4 μm thick | 30             | > 240          | 0.05  |
| 13     | HDPE              | EVA                   | 30           | 30             | 30 (±2.3)      | 2.6 ± 0.1   |
| 14     | Polypropylene     | None                  | 0            | 30             | 30 (±3.1)      | 1.9 ± 0.1   |
| 15     | Polybutylene      | None                  | 0            | 30             | 50 (±4.5)      | 1.3 ± 0.1   |

<sup>a</sup> LDPE—low density polyethylene, HDPE—high density polyethylene.

<sup>b</sup> Additives of metal and other component were incorporated during film production, excluding aluminum which was coated on a produced film; Cu—copper additive; EVA—ethylene-vinyl acetate.

plastic films. Barrier films reduce gas emissions from agricultural uses to the atmosphere, extend the period of degradation in the soil, and allow the use of reduced dosages without reducing the effectiveness of pest control. This approach has been examined and verified in several field experiments and under commercial farm conditions.<sup>2,17</sup> A reliable selection and use of appropriate impermeable films for soil fumigation is essential to ensure effective fumigation with reduced dosage and reduced emission. A few methods of testing plastic permeability to gases are known and used in the plastics industry.<sup>7-11</sup> The objective of the present study was to conduct a comparative test aimed at improving the selection of impermeable films.

Polyethylene-based films were permeable to MB as demonstrated by both methods (Table 2). Pronounced differences in permeability were recorded among LDPE films (Table 2), indicating production quality to be another major factor. In contrast, films with a layer of barrier material such as polyamide or EVOH were significantly less permeable as reflected by the parameters of permeability rate, TC<sub>90</sub> and lag-time as determined by the two testing methods, and other documented studies.<sup>18,19</sup>

When permeability rates of MB determined using the diffusion method and the variable volume methods were compared, a significant correlation was obtained with polyethylene-based films. This correlation was not significant with the impermeable films tested. The variable volume method is less sensitive and cannot detect permeability rates below 0.05 g m<sup>-2</sup> h<sup>-1</sup> whereas the dif-

fusion method can identify permeability rates as low as 0.0005 g m<sup>-2</sup> h<sup>-1</sup>. Some of the barrier films tested had permeability rates lower than that detectable by the variable-volume methods, and therefore accurate permeability rates could not be calculated. The two other permeability parameters, TC<sub>90</sub> and lag-time, also describe the permeability properties of films. Lower TC<sub>90</sub> and lag-time values indicate higher permeability of the films to MB, as observed for the polyethylene-based films (Table 2), whereas high values of these parameters were obtained with barrier films (Table 2). TC<sub>90</sub> and lag-time values describe two different parameters *via* two different testing methods, which do not appear to be related.

The diffusion and variable-volume methods differ in that the latter is more rapid and requires less equipment. On the other hand, it is less sensitive than the diffusion method, especially with low-permeability films. The variable-volume method can be useful in selecting barrier films, but the diffusion method should be selected for accurate permeability studies when low permeability is involved.

The permeability of all films increased with increased temperature, as evidenced with all tested permeability parameters (Table 2, Fig. 2). This was particularly evident with polyethylene films where permeability increased five- to six-fold when the temperature increased from 20 to 60°C. The effect of temperature on barrier-film permeability was less significant (Table 2). The first step of gas permeation through polymer films is a result of the solubility, the thermodynamic factor.<sup>12</sup>

An increase in temperature provides energy for enhancement of segmental motion. If the energy density is sufficient, the polymer may pass through structural transitions, such as the glass transition, which further affects solubility and diffusion processes. The effects of an increase in temperature may also be expressed in terms of the increase in free volume directly related to the bulk expansion of the polymer due to the increased segmental motion.<sup>12,20</sup> The effect of temperature on film permeability is important in terms of agriculture because fumigation with MB is often performed on warm clear days when plastic temperatures are as high as 50–60°C. In this case, only films which retain their barrier properties at high temperatures can be defined as giving a real barrier.

Film permeability to MB was affected by additives such as copper, the thickness and density of the polyethylene film (LDPE vs. HDPE), and the length of the monomer side-chains. The basic reason that polymers are permeable to fumigants is their relatively high level of segmental motion. The diffusion of the penetrant gas can be regarded as a sequence of diffusion steps during which the fumigant molecules pass through a potential barrier in the polymer. Diffusion of a given fumigant is therefore dependent on the polymeric chain segments. Side-chains, as in the case of polypropylene and polybutylene, and additives such as copper complex, increase the barriers to gas diffusion, thereby, reducing its permeation. In practice, however, the resultant reduction is not sufficient since permeability is still higher than the limit stated for impermeable films.

It should be noted that laboratory testing of film permeability is only the first step. Suitable mechanical properties of the films (e.g. film strength, resistance to tear) are most important in obtaining impermeable films suitable for agricultural uses. The methods described here do not take into account such properties. Thus, additional mechanical tests are needed to verify the agricultural suitability of such films. These include permeability tests in the field, in which plastic is laid down mechanically and gas retention under the film is measured under field conditions. Nevertheless, the initial selection described here is very important and effective as a first screening of impermeable films to be tested subsequently in the field. This first selection of barrier films, if performed properly, can reduce the number of expensive field experiments needed for their final selection.

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#### REFERENCES

1. Anon, Montreal Protocol on Substances that Deplete the Ozone Layer, *UNEP 1994 Report of the Methyl Bromide Technical Option Committee*. UNEP, Kenya, 1995, 304 p.
2. Gamliel, A., Grinstein, A., Peretz, Y., Klein, L., Nachmias, A., Tsrur, L., Livescu, L. & Katan, J., Reduced dosage of methyl bromide for controlling verticillium wilt of potato in experimental and commercial plots. *Plant Dis.*, **81** (1997) 469–74.
3. Munnecke, D. E., Kolbezen, M. J. & Wilbur, W. O., Types and thickness of plastic films in relation to MB fumigation. *Proc. Int. Agric. Plastic Congress*, San Diego, 1978, 482–7.
4. Pauly, S., Permeability and diffusion data. In *Polymer Handbook 3rd edn.* ed. J. Brandrup & E. H. Immergut. John Wiley & Sons, New York, 1985, pp. 435–49.
5. Wontner-Smith, T. & Chakrabarti, B., Measurement of permeability of plastic sheeting to fumigant gases. *International Pest Control*, **36** (1994) 15–17.
6. Klein, L., Methyl bromide as soil fumigant. In *The Methyl Bromide Issue*. ed. C. H. Bell, N. Price & B. Chakrabarti. John Wiley & Sons, New York, 1996, pp. 191–235.
7. Kamal, M. R., Jinnah, I. A. & Utracki, L. A., Permeability of oxygen and water vapor through polyethylene/polyamide films. *Polymer Engineering and Science*, **24** (1984) 1337–47.
8. Moyls, L., Hocking, R., Beveridge, T. & Timbers, G., Exponential decay methods for determining gas transmission rate of films. *Trans. ASAE*, **35** (1992) 1265.
9. Muthus, M., Marashimhan, K. S., Sharangapani, M. V. & Majumder, S. K., Transmission of methyl bromide and phosphine through fumigation tarpaulins. *International Pest Control*, **14** (1972) 12–16.
10. Phillips, G. I. & Nelson, H. D., Permeability to methyl bromide of plastic films and plastic- and rubber-coated fabrics. *J. Econ. Entomol.*, **50** (1957) 452–4.
11. Scheffrahn, R. H., Hsu, R. C. & Su, N. Y., Evaluation of polymer film enclosures as protective barriers for commodities from exposure to structural fumigants. *J. Agric. Food Chem.*, **38** (1990) 904–8.
12. Comyn, J., *Polymer permeability*. Elsevier Applied Science, London, 1986, 383 pp.
13. Anon, *Standard methods for determining gas permeability characteristics of plastic film and sheeting*. The American Society for Testing and Materials, D-1434, 1982.
14. Anon, *Standard test method for resistance of protective clothing materials to permeation by hazardous liquid chemicals*. The American Society for Testing and Materials, D-3985, 1985.
15. Kolbezen, M. J. & Abu el Haj, F. J., Permeability of plastic films to fumigants. *Proc. Int. Agric. Plastic Congress*, San Diego, 1978, 476–81.
16. Stern, S. A., Sinclair, T. F., Gareis, P. J. & Mohr, P. H., An improved permeability apparatus of the variable-volume type. *J. App. Polymer Sci.*, **7** (1963) 15–19.

17. Gamliel, A., Grinstein, A., Katan, J., Klein, L. & Ucko, O., Reducing dosage of methyl bromide by using virtually impermeable films and by combination with solarization. *Phytoparasitica*, **22** (1994) 163.
18. Houck, L. G. & Mackey, B. E., Permeability of flexible polymer films used to wrap citrus fruit to the fumigants ethylene dibromide and methyl bromide *J. Am. Soc. Hort. Sci.*, **114** (1989) 86–90.
19. Scheffrahn, R. H., Bodalbhai, L. & Su, N. Y., Nylon film enclosures for protection of foods from exposure to sulfur dioxide and methyl bromide during structural fumigation. *J. Agric. Food Chem.*, **42** (1994) 2317–21.
20. Daponte, T. L. F. Barrier films for soil fumigation. *Acta Hort.*, **382** (1994) 56–66.